

US-Russian Advances in Materials Science Conference
August, 30 – September, 4
Prague, Czech Republic

«Polymer Material Thermal Decomposition Model with Intensive Decomposition Area»

**Dr. Vladimir S. Sirenko,
Elena A. Egorova
VNIIA, Moscow, Russia**

Objective



- The polyurethane foams (PUF) and composites with epoxy matrix are used in protective coat structure.
- The analysis of materials response in conditions of different heating rates puts the objective of thermal decomposition mathematical model generation.
- Actual methods of model definition are based on activation equation systems, therefore equations quantity should be increased for appropriate experiment results reproduction.
- The increasing of activation equation quantity does not provide physically proved values of activation energy and preexponential factor, while the decreasing of this quantity causes significant instability of values.

Material Thermal Decomposition Model with Intensive Decomposition Area



- The increasing of decomposition material weight (concentration) as total differential:

$$dC = \left(\partial C / \partial t\right)_T dt + \left(\partial C / \partial T\right)_t dT.$$

At constant heating rate

$$dC / dt = \left(\partial C / \partial t\right)_T + \left(\partial C / \partial T\right)_t b,$$

T -temperature,

t -time,

$b = dT / dt$ - Temperature increment rate.

Material Thermal Decomposition Model with Intensive Decomposition Area



- **Main model areas:**
 - ➡ **Activation decomposition;**
 - ➡ **Polymer stability wastage and carbon producing process;**
 - ➡ **Carbon residue destruction.**

Model equation



Intensive decomposition:

$$\frac{m_0 - m_t}{m_t} = \left(\frac{T}{T_0} \right)^n$$

or

$$\frac{m_t}{m_0} = 1 / \left(1 + (T/T_0)^n \right) \quad (1)$$

at

$$T = T_{i\dot{a}\div} + \nu \cdot \tau \quad (2)$$

Residue decomposition:

$$\frac{m_t}{m_0} = \exp \left(- C \cdot \tau^k \right) \quad (3)$$

Table 1. Parameters of the polyurethane foam and fiberglass thermal decomposition model and coefficient of correlation between calculated and experimental values

Sample	Heating rate ν , °C/min	Expression parameters						Coefficient of correlation	
		1			3				
		T_0	n	\overline{n}	C	k	\overline{k}	$R(n,k)$	$R^*(\overline{n},\overline{k})$
PUF	20	386	12.4	13.0	0.671	0.264	0.211	0.9980	0.9929
PUF	50	408	13.5		0.943	0.160		0.9974	
PUF	100	432	13.1		1.225	0.268		0.9846	
FGEM	20	476	10.8	13.2	0.652	0.171	0.194	0.9974	0.9852
FGEM	50	489	13.2		0.827	0.165		0.9976	
FGEM	100	506	15.5		1.389	0.247		0.9978	
FGEM	100	503	14.7		1.361	0.334		0.9953	

The parameter analysis of thermal decomposition model in researched area displays:



- ➡ Discriminating temperature values T_0 , and C as well – are the material heating rate functions;
- ➡ For n & k values there is no definite functional dependence upon their determination conditions.

When calculating the values correlation coefficients, factors \bar{n} & \bar{k} were considered constant for each material and average in suitable range of heating rate, and T_0 & C values were taken as linear approximation:

- ➡ For PUF – $R^*=0,993$,
- ➡ For FGEM - $R^*=0,985$.

Functions of TGA experiment and fiberglass epoxy matrix model (model with equations (1), (2), (3))

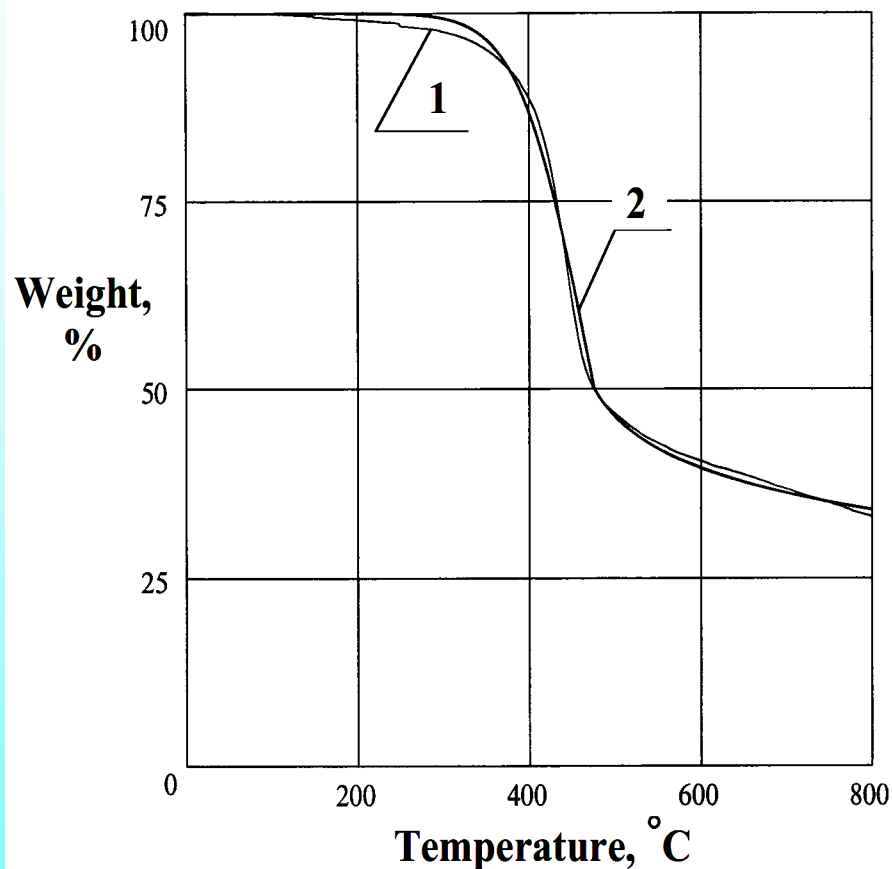


Figure 1. Experimental (1) and calculated (2) TGA curves at 20 °C/min heating rate.

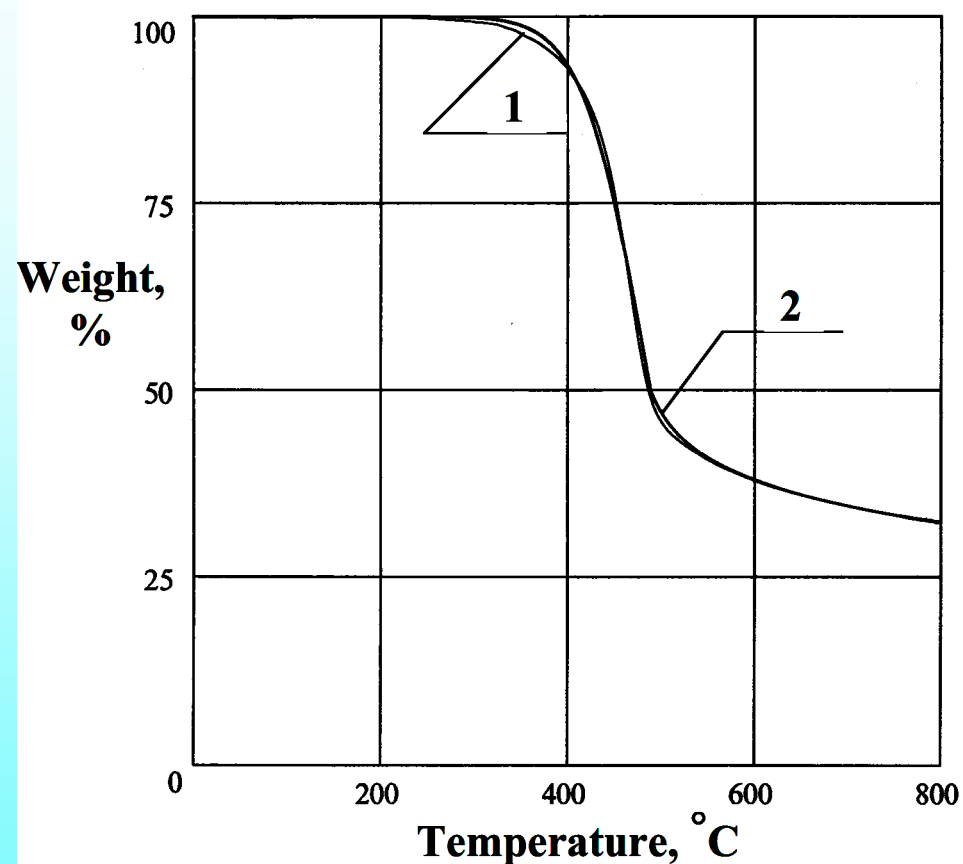


Figure 2. Experimental (1) and calculated (2) TGA curves at 50 °C/min heating rate.

TGA experimental and model functions for polyurethane by the equations (1), (2)

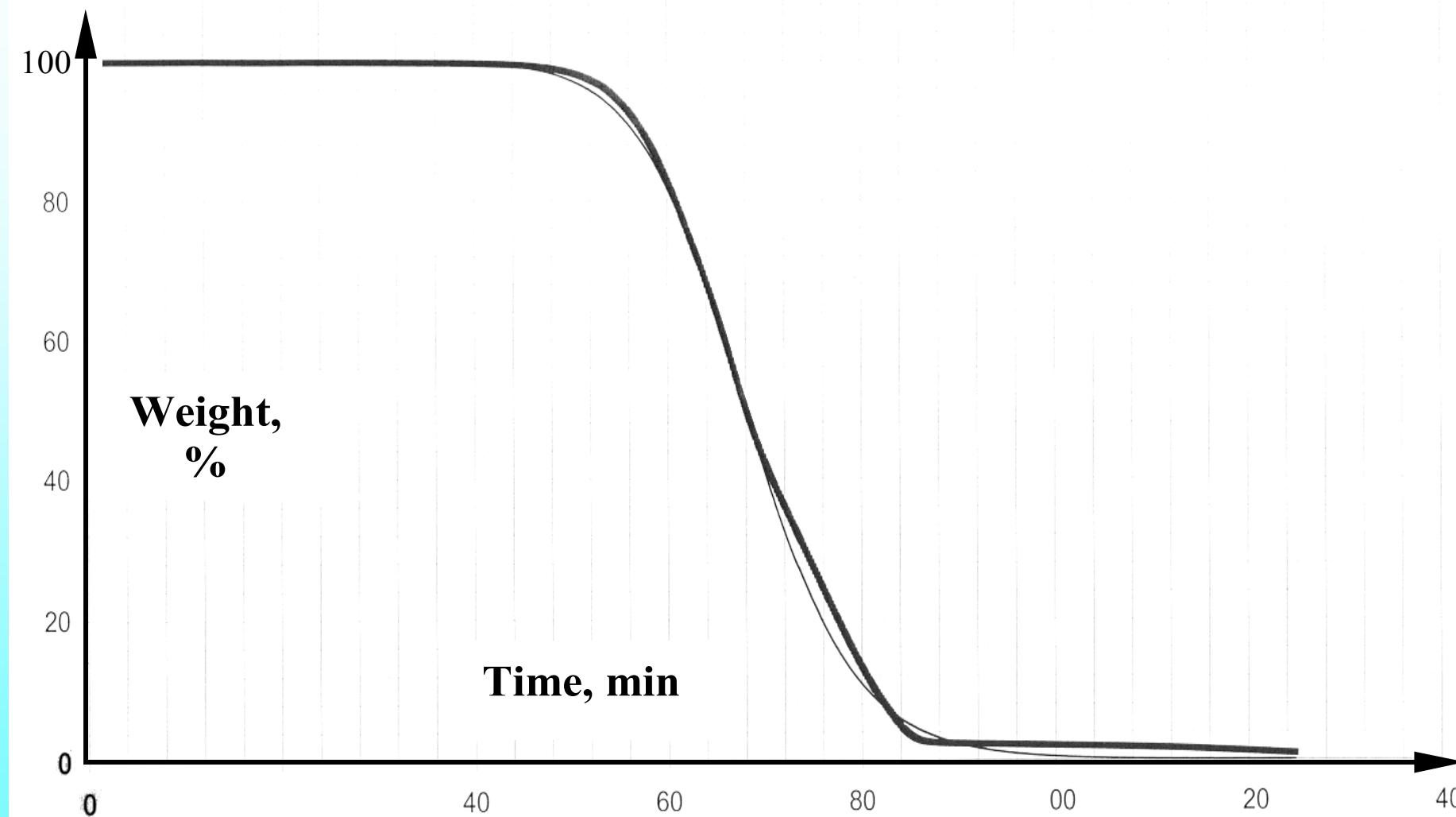


Figure 3. Experimental (thick) and calculated (thin) TGA curves for PU at 5 °C/min heating rate.

Conclusion



- The mathematical model was developed capable of describing the PUF and fiberglass thermogravimetric curves obtained at constant heating rates in the range 5-100 °C/min in inert atmosphere. Model characteristics depend upon chemical properties of tested polymers.
- Coefficients of multiple correlation between calculated and experimental values for tested polymers are at least 0,985 and therefore validate suggested Material Thermal Decomposition Model.